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| 14. ABSTRACT This project focuses on understanding the basic principles of bipolar electrode (BPE) arrays for chem/bio sensing applications. During this project period, we developed a self-powered, microelectrochemical sensing platform that reports its output using an electrochromic display. Additionally, we have demonstrated a new method to fabricate very inexpensive BPE devices in less than one hour using wax printing to define the architecture, a paper substrate, and carbon paste electrodes. Finally, we fabricated and tested BPE arrays that span two microchannels and | | | | | |
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Report Title

W911NF-07-1-0330

Very Large Arrays of Bipolar Electrodes

Final Report

ABSTRACT

This project focuses on understanding the basic principles of bipolar electrode (BPE) arrays for chem/bio sensing applications. During this project period, we developed a self-powered, microelectrochemical sensing platform that reports its output using an electrochromic display. Additionally, we have demonstrated a new method to fabricate very inexpensive BPE devices in less than one hour using wax printing to define the architecture, a paper substrate, and carbon paste electrodes. Finally, we fabricated and tested BPE arrays that span two microchannels and discovered some very interesting principles that add value to this sensing technology. We also showed that the latter has excellent sensing capabilities. These studies are aimed at reducing the cost of sensors based on BPEs, while simultaneously increasing their simplicity and directing them toward targets of interest to the DoD.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

| <u>Received</u> | <u>Paper</u> |
|-----------------|---|
| 05/29/2013 | 10.00 Hong Liu, Richard M. Crooks. Determination of Percent Hemoglobin A1c Using a Potentiometric Method, Analytical Chemistry, (02 2013): 0. doi: 10.1021/ac3032228 |
| 05/30/2013 | 13.00 Francois Mavre, John A. Crooks, Byoung-Yong Chang, Richard M. Crooks, Kwok-Fan Chow. A Large-Scale, Wireless Electrochemical Bipolar Electrode Microarray, Journal of the American Chemical Society, (06 2009): 8364. doi: 10.1021/ja902683f |
| 05/30/2013 | 15.00 Kwok-Fan Chow, Francois Mavre, Richard M. Crooks. Wireless Electrochemical DNA Microarray Sensor, Journal of the American Chemical Society, (06 2008): 7544. doi: 10.1021/ja802013q |
| 05/30/2013 | 17.00 Rahul Dhopeswarkar, Richard M. Crooks, Ulrich Tallarek, Dzmitry Hlushkou. The influence of membrane ion-permselectivity on electrokinetic concentration enrichment in membrane-based preconcentration units, Lab on a Chip, (05 2008): 1153. doi: 10.1039/b800549d |
| 05/30/2013 | 12.00 Francois Mavre, Kwok-Fan Chow, Eoin Sheridan, Byoung-Yong Chang, John A. Crooks, Richard M. Crooks. A Theoretical and Experimental Framework for Understanding Electrogenenerated Chemiluminescence (ECL) Emission at Bipolar Electrodes, Analytical Chemistry, (08 2009): 6218. doi: 10.1021/ac900744p |
| 07/13/2012 | 1.00 Robbyn K. Anand, Stephen E. Fosdick, Ioana Dumitrescu, Richard M. Crooks. Pressure-Driven Bipolar Electrochemistry, Journal of the American Chemical Society, (04 2011): 4687. doi: 10.1021/ja111050h |
| 07/13/2012 | 8.00 Hong Liu, Richard M. Crooks. Paper-Based Electrochemical Sensing Platform with Integral Battery and Electrochromic Read-Out, Analytical Chemistry, (03 2012): 2528. doi: 10.1021/ac203457h |
| 07/13/2012 | 7.00 Richard M. Crooks, Hong Liu. Three-Dimensional Paper Microfluidic Devices Assembled Using the Principles of Origami, Journal of the American Chemical Society, (11 2011): 17564. doi: 10.1021/ja2071779 |
| 07/23/2012 | 2.00 Byoung-Yong Chang, Kwok-Fan Chow, Francois Mavre, Richard M. Crooks, John A. Crooks. Design and Operation of Microelectrochemical Gates and Integrated Circuits, Journal of the American Chemical Society, (11 2010): 15404. doi: 10.1021/ja107095z |
| 07/23/2012 | 3.00 Kwok-Fan Chow, Byoung-Yong Chang, John A. Crooks, Richard M. Crooks, Francois Mavre, Robbyn K. Anand, Derek R. Laws. Bipolar Electrodes: A Useful Tool for Concentration, Separation, and Detection of Analytes in Microelectrochemical Systems, Analytical Chemistry, (11 2010): 8766. doi: 10.1021/ac101262v |
| 07/23/2012 | 4.00 Byoung-Yong Chang, Brian A. Zacheo, Kwok-Fan Chow, Francois Mavre, Richard M. Crooks. A Sensing Platform Based on Electrodissolution of a Ag Bipolar Electrode, Journal of the American Chemical Society, (07 2010): 9228. doi: 10.1021/ja103715u |
| 07/23/2012 | 5.00 Stephen E. Fosdick, John A. Crooks, Byoung-Yong Chang, Richard M. Crooks. Two-Dimensional Bipolar Electrochemistry, Journal of the American Chemical Society, (07 2010): 9226. doi: 10.1021/ja103667y |
| 07/23/2012 | 9.00 Byoung-Yong Chang, Kwok-Fan Chow, John A. Crooks, François Mavr , Richard M. Crooks. Two-channel microelectrochemical bipolar electrode sensor array, The Analyst, (05 2012): 2827. doi: 10.1039/c2an35382b |
| 07/23/2012 | 6.00 Byoung-Yong Chang, Francois Mavre, Kwok-Fan Chow, John A. Crooks, Richard M. Crooks. Snapshot Voltammetry Using a Triangular Bipolar Microelectrode, Analytical Chemistry, (06 2010): 5317. doi: 10.1021/ac100846v |

TOTAL: 14

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Georgia State University (Atlanta, GA, November, 2012) "Bipolar electrodes: concentration, separation and detection in microelectrochemical systems"

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

05/29/2013 11.00 Kyle N. Knust, Karen Scida, Stephen E. Fosdick , Richard M. Crooks. Bipolar Electrochemistry, Angewandte Chemie International Edition (02 2013)

TOTAL: 1

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> | Discipline |
|------------------------|--------------------------|------------|
| Morgan Anderson | 1.00 | |
| Hong Liu | 1.00 | |
| Stephen Fosdick | 1.00 | |
| FTE Equivalent: | 3.00 | |
| Total Number: | 3 | |

Names of Post Doctorates

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| Hong Liu | 1.00 |
| FTE Equivalent: | 1.00 |
| Total Number: | 1 |

Names of Faculty Supported

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| FTE Equivalent: | |
| Total Number: | |

Names of Under Graduate students supported

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| FTE Equivalent: | |
| Total Number: | |

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

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|--|------|
| The number of undergraduates funded by this agreement who graduated during this period: | 0.00 |
| The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... | 0.00 |
| Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... | 0.00 |
| Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: | 0.00 |

Names of Personnel receiving masters degrees

| <u>NAME</u> |
|----------------------|
| Total Number: |

Names of personnel receiving PHDs

| <u>NAME</u> |
|----------------------|
| Hong Liu |
| Total Number: |

Names of other research staff

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| FTE Equivalent: | |
| Total Number: | |

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Report

Project period covered by this report: 1 June 2007 – 28 February 2013

Project title: Very Large Arrays of Bipolar Electrodes

Project number: W911NF-07-1-0330

PI: Richard M. Crooks

Excellent progress was made during the five-year grant period. While each annual report spells out the technical progresses made in greater detail, this final report summarizes the highlights of advancements made during this project.

Introduction. The objective of this project was to develop the fundamental principles and technological innovations necessary for implementation of a very simple, light-weight, low-power electrochemical array sensing technology that has the sensitivity and limits of detection required to compete with fluorescence-based methods. There are three compelling reasons that justified this objective.

- Array-based chemical and biosensors are necessary for detection of WMDs.
- At present there are no viable, large-scale electrochemical array technologies.
- The project has immediate implications for impacting human health and environmental monitoring.

Our approach to achieving this objective was to employ arrays of bipolar electrodes (BPEs) that both sense and report the presence of target analytes. There are two key reasons for selecting BPEs. First, the electrochemical properties of many (thousands, or perhaps millions) BPEs can be controlled with just two driving electrodes. This greatly reduces the complexity of the sensing platform. Second, current passing through the BPEs, which signals the presence of the target, can be monitored optically using either electrogenerated chemiluminescence (ECL) or Ag electrodisolution. These detection methods allow many BPEs to be monitored simultaneously.

Microelectrochemical arrays based on bipolar electrodes. We demonstrated that medium-scale, wireless, electrochemical microarrays could be constructed from 1000 individual bipolar electrodes (BPEs). All 1000 electrodes in the microarray were controlled with just two driving electrodes and a simple power supply. The system was designed to have faradic reactions occurring at the cathode end of each electrode correlated to light emission via ECL at the anode end. Importantly, this made it possible to read out the ECL signal from the entire array simultaneously. The electrode array was fabricated on a glass microscope slide and operated in a very simple electrochemical cell. The significance of this design was that it provided a fabrication route to arbitrarily large electrode arrays and made it possible to place sensing chemistries onto each electrode using a robotic spotter (a task we were actively pursuing).

We were able to demonstrate the uniformity of ECL emission from each electrode in a micro array. This is important, because it suggests that each electrode has been subjected to a uniform electric field. Our analysis shows that the ECL intensity emitted from each bipolar electrode is about 3877 ± 374 counts. This confirms that the rate of faradaic reactions occur at each bipolar electrode is nearly the same.

Fundamental aspects of bipolar electrodes. We sought to better understand the fundamental principles governing the electrochemical properties of bipolar electrodes (BPEs). Specifically, we investigated how the emission of ECL at the anode end of a BPE is related to sensing chemistry present at the cathode end. Accordingly, a series of experiments was designed to determine the amount of current passing through a BPE, and how this current was related to the ECL emission intensity. In principle, a BPE is equivalent to two externally connected band electrodes, a configuration we call a split bipolar electrode. Therefore, we designed this type of device and inserted an ammeter between the two microband electrodes comprising

the BPE. We believed this would make it possible to directly relate current to the ECL emission intensity, which is the most critical parameter associated with this type of sensor.

The microchannel was filled with $\text{Ru}(\text{bpy})_3^{2+}$ and TPrA, and a potential difference (E_{tot}) was applied across a pair of driving electrodes present in reservoirs at the two ends of the microchannel. When E_{tot} was large enough, $\text{Ru}(\text{bpy})_3^{2+}$ and TPrA were oxidized at the anode side of the split bipolar electrode and the resulting current was read on the ammeter. Thus, the current flowing through the bipolar electrode can be recorded as a function of the external applied potential. Simultaneously, the ECL emission from the anode end of the BPE was measured.

To experimentally confirm the congruency of the split and continuous BPEs, one of each design was placed side by side in the same channel during measurements and the ECL emission from each was measured. The ECL intensities from both designs were found to be nearly the same.

From an analytical perspective, it is important to know the minimum amount of current required to generate a detectable ECL signal from a bipolar electrode (i.e., the limit of detection of the device). The aforementioned experiment can be used to make this measurement, and the results indicated a threshold current of $\sim 32 \text{ mA/cm}^2$ is required. Thereafter, the ECL intensity increases linearly as a function of the faradaic current passing through the BPE. The key finding of this part of the study was that because there is a direct relationship between current and ECL emission, BPEs can be used for quantitative chemical and biological sensing applications.

Snapshot voltammetry. When an electric field was applied across a microchannel containing buffer, the axial potential drop was, to a first approximation, linear. However, the potential of a bipolar electrode (BPE) within the channel is uniform over its entire surface, because it is a near-zero-resistance conductor. Consequently, the potential difference at the interface between the buffer solution and the electrode is a function of the axial position. It is this potential gradient that drives faradaic electrochemical reactions at BPEs.

In this part of our study, we used the linear potential gradient across a BPE as a means of simultaneously determining current as a function of potential. This is the classical voltammetry experiment, but here the entire voltammogram is captured in an instant. In analogy to spectroscopy, this advance is equivalent to the throughput improvement realized when photomultiplier tubes were replaced by CCD cameras. In the former case, long scan times (on the order of a few minutes) were required to obtain an entire spectrum, but the advent of CCDs cut this time to milliseconds. Indeed, here we used a CCD camera to determine the current flowing through different parts of the same electrode in just 1.5 s. This can be compared to the several minutes required to capture a typical voltammogram. The advantage of this approach for high-throughput analysis is obvious, as is the application to rapid detection of chemical and biological weapons.

Ag dissolution reporting on bipolar electrodes. In this segment we reported a new type of sensing platform that was based on electrodisolution of a metallic bipolar electrode (BPE). When a reduction reaction occurs at the cathodic end of the BPE, it triggers the oxidation and dissolution of Ag metal present at the anodic pole. The loss of Ag is easily detectable with the naked eye or a magnifying glass and provides a permanent record of the electrochemical history of the electrode. More importantly, the decrease in the length of the BPE can be directly correlated to the number of electrons passing through the BPE and hence to the sensing reaction at the cathode.

We showed that a split BPE is an effective tool for exploring critical electrochemical properties of wireless BPEs. Therefore, we employed the split BPE design to understand the operation of Ag/Au BPEs. Ag/Au BPEs were composed of a 5 nm Cr adhesion layer covered by 100 nm of Au, and they had

a length of 1.0 mm and a width of 0.25 mm. 5 nm of Cr and 20 nm of Ag overcoated the anodic pole. The split BPE was used to correlate the charge passing through the BPE to the extent of electrodisolution (the observable). To demonstrate the Ag dissolution, a microchannel was filled with 1.0 mM *p*-benzoquinone in 0.10 M acetate buffer at pH 5.5. A driving voltage (E_{tot}) of 12 V was applied across the 12 mm-long channel. After 290 s of operation, the driving voltage was removed and the lengths of the three BPEs were reduced to 0.797 ± 0.005 mm. The reproducibility of < 1% is remarkable. This shows that there is a linear relationship between the length of the Ag/Au BPE and the experimentally measured charge. This is important, because it means that BPEs based on the principle of electrodisolution can be used for quantitative sensing applications. Also, the anodic pole of the BPE was investigated using a scanning electron microscope outfitted with an energy dispersive X-ray system (SEM-EDS).

We have also demonstrated the individual addressability of the Ag/Au BPE system by selectively modifying BPEs next to an unmodified BPE. By using electrocatalytic amplification, we demonstrated Ag dissolution in the presence of target DNA. The importance of this experiment is to demonstrate that the Ag/Au BPE can be specifically modified for DNA hybridization or recognition reactions. The key finding of this project is that a BPE array can be remarkably sensitive but still read-out via the naked eye.

Medium-scale arrays of Ag dissolution bipolar electrodes. Our previous reporting mechanism for large microarrays of wireless BPEs depended on ECL from the simultaneous oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ and tri-*n*-propylamine. This reaction required a significant electric field to be applied such that the potential drop over each electrode, ΔE_{elec} , exceeds 1.3 V. For the array design described previously, the BPEs were 500 μm long and applied potential (E_{tot}) between the driving electrodes was 85 V. Because Ag oxidation is more thermodynamically favorable than ECL, the E_{tot} required for Ag dissolution reporting is much lower.

To demonstrate this concept, we fabricated microarrays of 100 Ag/Au BPEs on a single device. The BPEs consisted of 100 nm Au over a 5 nm Cr adhesion layer and were 500 μm in length and 50 μm wide. One half of each BPE (250 x 50 μm) was overcoated with 5 nm Cr and 20 nm Ag. The cell employed two parallel stainless steel driving electrodes within a Teflon holder. The solution volume of the cell was limited using poly(dimethylsiloxane) (PDMS) blocks so that solution connected the two driving electrodes and covered the entire array. By coupling Ag dissolution to the reduction of *p*-benzoquinone to hydroquinone, we determined that driving potentials as low as 30 V were needed to realize Ag dissolution in this array format.

Two-dimensional bipolar electrochemistry. We demonstrated the concept of two-dimensional bipolar electrochemistry and its principle of operation. An interesting result of this research is that electrochemical reactions can be localized at particular locations on the perimeter of a two-dimensional bipolar electrode (2D-BPE), configured at the intersection of two orthogonal microfluidic channels, by controlling the electric field within the contacting electrolyte solution. Experimentally determined maps of the electric field in the vicinity of the 2D-BPEs are in semi-quantitative agreement with finite element simulations.

We took a 2D-BPE [1.75 x 1.75 mm square] Au BPE and located it at the intersection of two microfluidic channels. When two independent driving potentials (E_{tot1} and E_{tot2}) were applied across the two channels, the resulting potential gradient in solution was the vector sum of E_{tot1} and E_{tot2} in the microfluidic space. The interfacial potential difference between the solution and 2D-BPE, the driving force for electrochemical reactions, was therefore a function of location. This made it possible to focus electrochemical reactions at specific points on the 2D-BPE. When a potential of 20.0 V (E_{tot1}) was applied across the horizontal channel, ECL results from the simultaneous oxidation of tri-*n*-propylamine and $\text{Ru}(\text{bpy})_3^{2+}$. A potential applied across the second channel moved the ECL reaction around the perimeter of the 2D-BPE depending on the direction of the vector sum of the two potentials. When E_{tot1} and E_{tot2}

were applied, the greatest potential gradients occurred at the intersection of oppositely polarized channels. We experimentally mapped the non-uniform electric field using ECL from four 64-element BPE arrays situated just outside the channel crossing. Because the intensity and area of ECL reporting is dependent on the magnitude of the potential drop over that electrode, we were able to determine the nature of the two-dimensional electric field. We then compared this to finite element simulations that were in semi-quantitative agreement with experimental results. The significance of this work was that we can wirelessly control the location of faradaic reactions on a conductive substrate in a microfluidic device. By comparing the experimentally determined electric field map based on ECL intensities to those of finite element simulations, we were able to describe where electrochemical reactions would occur on the 2D-BPE.

Pressure-driven bipolar electrochemistry. We reported a method for driving bipolar electrochemistry in the absence of an externally applied voltage. In this section of research, the driving force was the streaming potential generated from pressure-driven flow in a microfluidic channel with charged walls. Streaming potentials ranged from tens of millivolts to volts, values which are sufficient to drive electrochemical reactions at the anodic and cathodic poles of a bipolar electrode (BPE) present in the microfluidic channel. We demonstrated the faradaic nature of the current flowing through a split BPE (i_{BPE}) by following the anodic electrooxidation of Ag coupled to the reduction of *p*-benzoquinone (BQ) at the BPE cathode. The key result from this work was that pressure-driven flow alone, with no external power supply, can be used to drive bipolar electrochemistry. This result bodes well for low-current sensors that can be easily powered in remote locations without electricity.

The importance of this work, was that bipolar electrochemistry can be achieved in the absence of an external electrical power source. Indeed, the pressures employed are sufficiently low that they can be easily generated using a manually operated syringe. Moreover, Ag electrodisolution can be visualized with a simple magnifying device, which further simplified this type of device for sensing applications that are coupled to a redox event at the cathodic pole of the BPE.

Bipolar electrodes for rapid screening. We investigated the use of BPEs as a platform for screening new chemically selective interfaces. The initial proof-of-concept experiments were focused on determining the relative activity of electrocatalysts for the oxygen reduction reaction (ORR), but our ultimate goal was to screen interfaces that will be selective for particular redox-active targets. These experiments were carried out by coupling the dissolution of Ag at the anodic pole of a BPE to the ORR on the cathodic pole. By immobilizing catalyst materials having differing activities for the ORR, it will be possible to differentiate their efficiency by comparing the change in length of the Ag film. This will allow rapid screening of the electrocatalysts, because (as we discovered earlier in this project) many BPEs can be controlled simultaneously without direct electrical contact.

Specifically, when a BPE was in contact with a solution supporting an electric field, then the potential dropped over the BPE (ΔE_{elec}) was determined by the applied voltage (E_{tot}) and the ratio of the length of the BPE (l_{elec}) to the distance between the driving electrodes (l_{channel}). When E_{tot} was applied, the length of the BPE changed due to the oxidation of Ag. The anodic dissolution of Ag stopped when the potential dropped over the electrode was insufficient to drive the two electrically coupled faradaic reactions (i.e., the ORR and Ag oxidation). The overpotential required to drive the ORR on Pt was much lower than it was for Au. To this end, we selectively modified several BPEs by dropcasting nanoparticles (NPs) onto the cathodic poles. We were able to show a proof-of-concept experiment where Pt and Au NPs demonstrated different activities for the oxygen reduction reaction as determined by the distinct differences in the final lengths of the Ag film on each BPE.

Two-channel bipolar electrode array. We developed an interchannel BPE sensor that communicates between separate sensing and reporting microchannels where the opposing poles of the BPE were embedded in separate fluid-filled microchannels. A driving voltage applied across the two microchannels wirelessly induced a potential difference (ΔE_{elec}) across the BPE that drove faradaic reactions at the BPE's poles if ΔE_{elec} was sufficiently large. In this manner, faradaic current can be transmitted between separate microchannels through the BPE. In our experiments the sensing pole rested in a microchannel containing an electroactive target species. Upon electrochemical reduction of the target species, a detection signal was transmitted from the sensing to the reporting pole, where electrogenerated chemiluminescence (ECL) indicated the target's presence.

Compared to the single channel sensors reported by our group, the key advantage of multichannel architecture was the separation of ECL reporting species from the target materials. Multiple channels prevented ECL species and ECL byproducts from disrupting the target chemistry and ensured that the target molecules could not quench or interfere with the ECL pathway. Tuning the design of individual electrodes within such arrays also dictates the array's output. By modulating the lengths of bipolar electrodes, arrays may be fabricated to deliver identical or radically different potentials to individual electrodes in the array from a single driving potential. A practical application of an interchannel bipolar electrode array was also demonstrated using surface-modified bipolar electrodes to detect glycated hemoglobin (HbA_{1c}), which is the most important index for measuring the long-term average blood glucose level in the human body.

Paper-based electrochemical sensing. At the point in the project, we began transition of our studies of electrochemical sensing devices toward practical applications. We are particularly sensitive to the DoD need for low-cost, low-power portable sensing devices, and these metrics were very well aligned with the approaches we had developed during the first several years of funding. Accordingly, we developed a battery-powered, microelectrochemical sensing platform that reports its output using an electrochromic display. The platform was fabricated using paper fluidics and incorporates a Prussian blue spot (1.2 mm in diameter) electrodeposited on an indium-doped tin oxide thin film as the electrochromic indicator. The integrated Al/air battery (0.95 V) powered both the electrochemical sensor and the electrochromic read-out, which are in electrical contact via a paper reservoir. We showed that a piece of Reynolds Wrap Al foil could be used as the anode for the sensors. The per-sensor cost of the foil is \$US 0.00006, and the total cost for each battery, including the ITO current collectors, is \$US 0.95.

The device operates as follows. An aliquot of artificial urine is introduced to activate the battery and the presence of analyte in the sample initiates the color change of the Prussian blue spot. The diameter of the spot is correlated to the detection limit of the sensor and can be adjusted to meet clinical threshold values. The entire system is assembled on the lab bench, without the need for cleanroom facilities. The applicability of the device to point-of-care sensing is demonstrated by qualitative detection of 0.1 mM glucose and H₂O₂ in artificial urine samples.